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REGULAR ARTICLE

Computational modeling of extended systems

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Abstract Advancements in computing architecture and in theoretical techniques allow for the modeling of complex, extended systems. This section of the 50th anniversary issue of *Theoretical Chemistry Accounts* highlights modeling work performed on nanostructured systems and underscores the enormous potential for synergy between theory and experiment in modern nanoscience.

Keywords Advances in computer architecture · Synergy between nanoscience theory and experiment · Molecular lines on silicon · Nanoparticle-polymer nanocomposites · Protein crystal structure modeling by density-functional theory

"What a wonderful time to be a computational chemist". One may speculate that that was the sentiment of the scientists that first published in *Theoretica Chimica Acta*, the progenitor of *Theoretical Chemistry Accounts*. In 1962, Fritz Grein (a new professor of theoretical chemistry at the University of New Brunswick in Canada)[1] published a paper in German, one of the four accepted languages for papers published in the journal, on the use of one-center wave functions for the study of symmetric BH_4^-, CH_4, and NH_4^+ in the 50-year-old issue of *TCA* [1]. Grein used a Royal Precision LGP-30 for his calculations, a machine that was referred to as a mobile "desk computer". These descriptors of the LGP-30 were indeed accurate: The 800-pound computer was the size of a desk and it had wheels so that it could be rolled from room to room [2]. Professor Grein recently recounted that the computer was "unbelievably slow by today's standards," but it was nevertheless a critical tool for his research. Computers have come a long way since 1962,[2] as have the theoretical methods we use for simulations. Cutting-edge modeling tools have been built to take advantage of new architectures, such as graphics processing units [3, 4][3], and are able to provide valuable information about large systems.

The central role of quantum chemical simulations in most areas of modern research has much to do with the remarkable growth in nanoscience over the last decade. There has been a convergence in the ability to perform experiments on nanosized objects (viz., atom-resolved microscopy, single-molecule experimental techniques, etc.) with advances in computing capability and in theory and simulation techniques. This convergence has resulted in unprecedented synergy between computational scientists and experimental physicists/chemists and engineers in

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[1] Professor Grein is now a retired (but still active) professor of theoretical chemistry at the University of New Brunswick (Fredericton). He was invited to contribute to the first issue of *Theoretica Chimica Acta* by his PhD supervisor, Hermann Hartmann, who started the journal.

[2] For example, the computational infrastructure at the National Institute for Nanotechnology consists of 1140 conventional CPU-cores with 32 GPU nodes housed in four interconnected racks. Each rack has wheels (for mobility), and the entire system weighs about 11 times *more* than the LGP-30.

[3] The Theoretical and Computational Biophysics Group at the University of Illinois at Urbana-Champaign has developed a version of NAMD, a classical molecular dynamics package, to take good advantage of GPUs to accelerate certain part of the program.

efforts ranging from the creation of novel materials to the development of devices based on molecular electronics.[4]

The contributions to this section of the special issue illustrate the diversity of approaches to treating extended systems and their relevance to modern nanosystems. The work of Smeu, Wolkow and Guo [5] demonstrates the use of a non-equilibrium Green's function approach combined with density-functional theory (NEGF-DFT) to predict and visualize how current passes through molecular nanostructures that are formed in a self-directed fashion on semiconducting silicon surfaces. Nanosystems of this type may allow for the exploitation of the tunable properties of organic species with technologically ubiquitous silicon. Earlier experimental and computational work on similar nanostructures suggested they may be used as new models for molecular transistors [6] and to create self-assembled molecular "circuit" patterns [7]. The results of Smeu et al. provide insights into how substituents might be used to cause current to flow through the molecular assemblies rather than through the silicon substrate and thereby offers much needed guidance in the construction of novel, molecule-based electronic devices.

In the work of Rowen and Paci [8], DFT is used in combination with molecular dynamics simulations to predict how the optical properties of silver nanoparticles (NPs) embedded in polymer matrices depend on the size, shape and other physical properties of the particles. Nanoparticle-polymer composites hold much promise for creating novel materials that combine the tunability associated with NPs with the desired mechanical properties of polymers. Methodologies for controlling metal nanoparticle morphology are now well developed [9], allowing for control over their properties. Well-organized distributions of NPs a bulk polymers allows materials with carefully engineered and well understood properties to be assembled [10].

The contribution of Falklöf, Collyer and Reimers [11] discusses an important element in their group's effort to develop a first-principles DFT approach to protein X-ray crystal structure refinement. Recent studies have shown that there are problems with standard refinement procedures when they are applied to systems with unusual components (see the manuscript of Falklöf et al. for details). For this reason, the use of computational approaches that do not rely on classical mechanical force-field type parameterization are desirable, and the use of quantum mechanical methods in this connection has been shown to improve protein structure prediction [12].

In closing, this section of the 50th anniversary issue of *Theoretical Chemistry Accounts* celebrates the great advancements in the modeling of extended systems and showcases novel approaches to predicting the properties of nanoscale systems. The advances in theoretical approaches and in computing capability have given us the ability to engage in research never before thought possible, making this a truly wonderful time to be a computational chemist.

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